

Significant Structure of Liquid Water

by

Hyungsuk Pak and Seihun Chang

Dept. of Chem. Seoul Natl. Univ., Korea.

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물의 구조와 성질

서울대학교 문리과대학 화학과

박형석·장세헌

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요 약

물은 용융점, 끓는점, 용융열 및 증발열등이 수소와 6족원소와의 화합물의 성질로부터 예측되는 값보다 훨씬 크고 ice-I이 녹을 때 부피의 감소가 일어나는 등 특이한 성질을 가지고 있다. 이와같은 성질들을 정량적으로 설명하려고 지금까지 많은 연구자들이 노력해 왔다.

저자들은 물의 큰 표면자유에너지와 용융시의 특수한 부피변화로 미루어 물의 구조모형을 다음과 같이 생각하였다. 즉, 얼음이 용융함에 따라 분자크기의 이동성 빈자리가 도입되면 물의 큰 표면에너지 밀도로 말미암아 빈자리 주위의 물분자는 촘촘한 배열을 가지게 되며 빈자리에서 떨어져있는 분자는 ice-I의 구조를 가질것으로 생각된다. 빈자리 주위의 분자가 빈자리에 뛰어 들어갈 때는 이동자유도를 지니게 될 것이다. 저자들은 H. Eyring의 액체구조이론을 써서 물의 liquid partition function을 위에 말한 바와 같은 구조모형로부터 유도하고 물의 증기압, 용융 및 증발엔트로피등 여러가지 열역학적 성질 및 물부피를 계산하여 실험치와 좋은 일치를 얻었다.

Abstract

Water has the melting point, the boiling point, the heat of fusion, and the heat of vaporization all much higher than would be normally expected from the hydrogen compounds of the other members of the oxygen family. Another unique characteristic of ice-I is its volume decrease which takes place in its melting. A number of significant efforts have been made in the past to explain these properties quantitatively.

The authors, reasoning from the unusually great free surface energy of water and the characteristic volume change on melting, propose the structural model of liquid water as follows. On melting, fluidized vacancies of a molecular size are introduced. Thereupon, for the unusually great surface energy density, molecules surrounding the vacancies become to have close packed arrangement. But molecules not in direct contact with vacancies should still possess the original structure i.e., ice-I. When a molecule adjacent to a vacancy jumps into the vacancy, the molecule attains the gaslike degree of freedom. Using the above model, the authors had developed the liquid partition function of water by applying the theory of significant structures in liquids. Molar volume, vapor pressure, entropy of fusion and entropy of vaporization were calculated over a wide temperature range. The results show good agreement with experimental observations.

Introduction

Water has several abnormal physical properties in its higher melting point, boiling point, heat of vaporization and heat of fusion than would be normally expected from the hydrogen compounds of the other members of the oxygen family. Likewise, the density of this substance change abnormally with temperature.

Many efforts have been made to quantitatively explain such properties of water^{(1) (2)}, however, none of the single approach has been fully satisfactory.

Recently, H. Eyring and R. P. Marchi have reviewed the significant liquid structure theory and in it they proposed a partition function of water⁽³⁾. They assumed that liquid water may have two different solid like structures, the one being the tetrahedrally hydrogen-bonded molecule and the other being the freely rotating monomer, the latter rotating in the interstitial sites of the former. But viewing from the molar volumes they have given for each of these different structures i. e., $V_{s1}=17.61$, $V_{s2}=17.11$ ml/mole, it is impossible to explain that these two structures are interstitially superimposed. Also, such solid like molecules cannot be expected to rotate freely in interstitial sites.

Nevertheless, the significant liquid structure theory has been very helpful to illustrate the properties of various liquids. The success of the theory in explaining the properties of various liquids show the promise of its application to liquid water, and it has been the author's aim to describe the model of liquid water as described below.

model

In the significant liquid structure theory Chang and co-workers have assumed that the solid like molecules in liquid may have different structure from that of the solid itself⁽⁴⁾.

For liquid water, the authors had assumed that there are two forms of solid like structures, α - and β -forms, unlike in other liquids.

For ice-I, the authors assume that when it melts, the structure is not completely destroyed for the strong hydrogen bonding. And the structure is gradually destroyed as the temperature rises. As liquid water is formed from the melting of ice-I, the structure of which is to be referred hereafter as the α -form, fluidized

vacancies are introduced according to the significant liquid structure theory.

For the extraordinarily high density of surface energy of water, as the authors assume, molecules surrounding the vacancies should possess different structure. Molecules surrounding the vacancies should rather possess close-packed structure like ice-III, which is to be referred hereafter as the β -form. But molecules not in direct contact with vacancies should still possess the original structure i. e., the α -form.

The structural model of liquid water, as assumed, can be summarized as in the following.

(a) the molecules surrounding the vacancies have solid like degree of freedom of β -form, but owing to the vacancies they possess a positional degeneracy.

(b) dynamic vacancies of molecular size of β -form exist and when a molecule jumps into the vacancies, the molecule attains a gas like degree of freedom, the structure of which is to be referred hereafter as γ -form.

(c) the molecules which are not in contact with the vacancies have solid like degree of freedom of α -form and the positional degeneracy need not be considered as there exist only the short range molecular forces.

The above liquid model shows the picture of an instantaneous state of water. As the vacancies move at random, molecules of water undergo instantaneous structural changes according to their relative positions to the vacancies.

From above, the liquid partition function for water is developed as in the following.

Partition function of a molecule of α -form

The Einstein model of solid can be used in the liquid range of temperature for α -form, because the molecules of α -form are not in direct contact with the vacancies. The hindered torsional oscillation of the molecule is approximated as a harmonic oscillation, and its frequency is taken equal to that of lattice vibration.

Thus, the partition function of a molecule of α -form, f_{α} , can be written as follows.

$$f_{\alpha} = \frac{\exp(E_{\alpha}/RT)}{(1 - \exp(-\theta_{\alpha}/T))^3} \prod_{i=1}^3 \frac{1}{(1 - \exp(-h\nu_i/kT))} \quad (1)$$

where E_{α} is the ground state energy and θ_{α} is the Einstein characteristic temperature for the α -form. The interatomic vibrational frequencies, ν_i , in a molecule

can be taken as the same for the three forms without appreciable errors.

Partition function of a molecule of β -form.

The Einstein solid model can also be used for β -form, but due to the fluidized vacancies a certain amount of strain is produced. The effect is to change the potential energy of β -form and create positional degeneracy equal to the number of the vacancies, n_v , which are accessible to a molecule in addition to its single most stable position, multiplied by the probability that the molecule has enough energy, ε , to move into one of these sites. Therefore, the total number of positions available to a molecule of β -form is $1+n_v \exp(-\varepsilon/kT)$

Then, the partition function of a molecule of β -form, f_{β} , is written as

$$f_{\beta} = \frac{\exp(-\theta_{\beta}/T)}{(1-\exp(E_{\beta}/RT))^6} \frac{1}{\prod_{i=1}^3 (1-\exp(-h\nu_i/kT))} [1+n_v \exp(-\varepsilon/kT)] \quad (2)$$

where E_{β} is the ground state energy of β -form and θ_{β} is the Einstein characteristic temperature. The frequency of the hindered torsional oscillation is taken equal to that of lattice vibration.

Partition function of a molecule of γ -form

When a molecule jumps into the vacancies it has a gas like degree of freedom. Associated molecules in the liquid state cannot have the gas like degree of freedom, because the vacancies are only of molecular size of β -form. Therefore, it is reasonable to assume that only monomers can be γ -form. Then, the partition function of a molecule of γ -form, f_{γ} , is given as

$$f_{\gamma} = \frac{(2\pi mkT)^{3/2} V_f}{h^3} \frac{\pi^{1/2}}{2} \frac{(8\pi^2 kT)^{3/2} (I_A I_B I_C)^{1/2}}{h^3} \frac{1}{\prod_{i=1}^3 (1-\exp(h\nu_i/KT))} \quad (3)$$

where V_f is the free volume available to the molecule of γ -form, that is, the total volume of the vacancies in a mole of liquid water and I_A , I_B , I_C are the principal moment of inertia and the others have the usual meanings.

Partition function of a mole of liquid water

If we know the partition functions f_{α} , f_{β} and f_{γ} and the fractions of the respective species ξ_{α} , ξ_{β} and ξ_{γ} in a mole of liquid water, and assuming the molecules of

γ -form are indistinguishable, we can describe the partition function of a mole of liquid water, F , with the following equation,

$$F = f_{\alpha}^{\xi_{\alpha} N} f_{\beta}^{\xi_{\beta} N} f_{\gamma}^{\xi_{\gamma} N} \frac{1}{(\xi_{\gamma} N)!} \quad (4)$$

where N is Avogadro's number. Using Stirling's approximation, F can be written as

$$F = f_{\alpha}^{\xi_{\alpha} N} f_{\beta}^{\xi_{\beta} N} \left\{ f_{\gamma} \frac{e}{\xi_{\gamma} N} \right\}^{\xi_{\gamma} N} \quad (5)$$

To know the fractions ξ_{α} , ξ_{β} and ξ_{γ} , molar volumes of liquid water, α -form and β -form are respectively taken as V , V_{α} and V_{β} .

If v_{α} is the volume occupied by α -form in a mole of liquid water, the same for β -form and γ -form can be expressed respectively as

$$V_{\beta} - v_{\alpha} \frac{V_{\beta}}{V_{\alpha}} \quad \text{and} \quad V - v_{\alpha} - (V_{\beta} - v_{\alpha} \frac{V_{\beta}}{V_{\alpha}})$$

Similarly, the total volume of a mole of liquid water when the volume occupied by a molecule of β -form and the vacancy are expanded to the size of a molecule of α -form can be obtained as

$$(V - v_{\alpha}) \frac{V_{\alpha}}{V_{\beta}} + v_{\alpha}$$

Now, the fraction of α -form, ξ_{α} , is given by

$$\xi_{\alpha} = \frac{v_{\alpha}}{(V - v_{\alpha}) \frac{V_{\alpha}}{V_{\beta}} + v_{\alpha}}$$

Then, the fractions of β -form and γ -form in the remaining fraction can be written respectively as

$$\frac{V_{\beta} - v_{\alpha} \frac{V_{\beta}}{V_{\alpha}}}{V - v_{\alpha}} \quad \text{and} \quad \frac{V - v_{\alpha} - (V_{\beta} - v_{\alpha} \frac{V_{\beta}}{V_{\alpha}})}{V - v_{\alpha}}$$

Therefore,

$$\xi_{\beta} = \left(1 - \frac{v_{\alpha}}{(V - v_{\alpha}) \frac{V_{\alpha}}{V_{\beta}} + v_{\alpha}} \right) \frac{V_{\beta} - v_{\alpha} \frac{V_{\beta}}{V_{\alpha}}}{V - v_{\alpha}}$$

and

$$\xi_{\gamma} = \left(1 - \frac{v_{\alpha}}{(V - v_{\alpha}) \frac{V_{\alpha}}{V_{\beta}} + v_{\alpha}} \right) \frac{V - v_{\alpha} - (V_{\beta} - v_{\alpha} \frac{V_{\beta}}{V_{\alpha}})}{V - v_{\alpha}}$$

Substituting,

$$\frac{V}{V_{\beta}} \equiv x, \quad \frac{V_{\alpha} - V_{\beta}}{V_{\beta}} \equiv s, \quad \frac{v_{\alpha}}{V_{\alpha}} \equiv \alpha \quad \text{and} \quad x - \alpha s \equiv u$$

then, the above fractions can be rewritten as,

$$\xi_{\alpha} = \frac{\alpha}{u}, \quad \xi_{\beta} = \frac{1-\alpha}{u} \quad \text{and} \quad \xi_{\gamma} = 1 - \frac{1}{u} \quad (6)$$

When the species are in equilibrium, the equilibrium constant, K , between α - and β -forms is given by

$$K = \frac{\xi_{\beta}}{\xi_{\alpha}} = \frac{f_{\beta}}{f_{\alpha}} \quad (7)$$

Therefore, from the partition functions f_α and f_β the equilibrium constant or the ratio $\frac{\xi_\beta}{\xi_\alpha}$ can be obtained.

The position degeneracy factor in the equation (2) can be given by the following expression. The number of vacancies, n_h , must be proportional to the ratio of ξ_γ and ξ_β , hence,

$$n_h = n \frac{\xi_\gamma}{\xi_\beta} = n \frac{u-1}{1-\alpha} \quad (8)$$

where n is the proportionality constant which is equal to the number of the nearest neighboring sites of a molecule in the liquid at the triple point. Since the molecules of β -form are close-packed, n is given by

$$n = 12 \times \frac{V_\beta - v_{at} \frac{V_\beta}{V_\alpha}}{V_t - v_{at}} = 12 \times \frac{1 - \alpha_t}{u_t - \alpha_t} \quad (9)$$

where V_t and v_{at} , respectively, are the molar volume of liquid water and the volume occupied by α -form in a mole of liquid water at the triple point which is taken as the ground state of liquid water.

The strain energy ϵ should be inversely proportional to n_h and directly proportional to E_β , and takes the form

$$\epsilon = \frac{aE_\beta}{n_h N} \quad (10)$$

where a is the proportionality constant.

Then, the liquid partition function of water is given by

$$F = \left[\frac{\exp(E_\alpha/RT)}{(1 - \exp(-\theta_\alpha/T))^6} \frac{1}{\prod_{i=1}^3 (1 - \exp(-h\nu_i/kT))} \right]^{\frac{\alpha N}{u}} \times \left[\frac{\exp(E_\beta/RT)}{(1 - \exp(-\theta_\beta/T))^6} \frac{1}{\prod_{i=1}^3 (1 - \exp(-h\nu_i/kT))} \right]^{\frac{1-\alpha}{u} N} \times \left[\frac{(2\pi mkT)^{3/2} V_\beta u}{h^3 N} \frac{\pi^{1/2}}{2} \frac{(8\pi^2 kT)(I_A I_B I_C)^{1/2}}{h^3} \frac{1}{\prod_{i=1}^3 (1 - \exp(-h\nu_i/kT))} \right] \left(1 - \frac{1}{u}\right)^N \quad (11)$$

Calculation

From the partition function, the following equations (12) can be derived for the calculation of the maximum work function, A ,

$$\varphi \equiv -\frac{A}{RT} = -\frac{1}{u} [\alpha \sigma_\alpha + (1-\alpha)(\sigma_\beta + y) + (u-1)(\gamma + \ln u)] \quad (12)$$

where

$$\sigma_\alpha = \frac{E_\alpha}{RT} - \sum_{i=1}^3 \ln(1 - \exp(-\theta_{\alpha i}/T)) \quad (12a),$$

$$\sigma_\beta = \frac{E_\beta}{RT} - \sum_{i=1}^3 \ln(1 - \exp(-\theta_{\beta i}/T)) \quad (12b),$$

$$y = \ln \left\{ 1 + n \frac{u-1}{1-\alpha} e^{-\omega} \right\} \quad (12c),$$

$$w = \frac{aE_\beta}{n \frac{u-1}{1-\alpha} RT} \quad (12d)$$

and

$$\gamma = \ln \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \frac{e}{N} \frac{\pi^{1/2}}{2} \frac{(8\pi^2 kT)^{3/2} (I_A I_B I_C)^{1/2}}{h^3} \frac{1}{\prod_{i=1}^3 (1 - \exp(-h\nu_i/kT))} \right\} + \ln V_\beta = \gamma' + \ln V_\beta \quad (12e)$$

And from the equations (1), (2) and (7), the equation (13) for the equilibrium constant is obtained.

$$\frac{\xi_\beta}{\xi_\alpha} = \frac{1-\alpha}{\alpha} \frac{\exp(E_\beta/kT)}{\prod_{i=1}^3 (1 - \exp(-\theta_{\beta i}/T))} \left\{ 1 + n \frac{u-1}{1-\alpha} e^{-\omega} \right\} \frac{\prod_{i=1}^3 (1 - \exp(-\theta_{\alpha i}/T))}{\exp(E_\alpha/RT)} = \frac{\prod_{i=1}^3 (1 - \exp(-\theta_{\alpha i}/T))}{\prod_{i=1}^3 (1 - \exp(-\theta_{\beta i}/T))}$$

$$\exp\{-(E_\alpha - E_\beta)/RT\} e^{\gamma} \equiv \text{rexp}\{-\Delta\theta E_t/RT\} e^{\gamma} \quad (13)$$

Transformations using equations (12) and (13) yield the following equation (14).

$$\varphi = \frac{1}{u} \left[\sigma_\alpha + (1-\alpha) \ln \frac{1-\alpha}{\alpha} + (u-1)(\gamma + \ln u) \right] \quad (14)$$

The equation (14) is the calculating form of the work function, A , of liquid water.

The vapor pressure, P , is given by

$$\frac{PV_\beta}{RT} = \left(\frac{\partial \varphi}{\partial x} \right)_T = \frac{1}{u-1} \left[\left\{ \left(s \frac{1-\alpha}{u-1} - 1 \right) \ln \frac{1-\alpha}{\alpha} - \frac{1}{\alpha} - \frac{s(u-1)}{u} \right\} \frac{\partial \alpha}{\partial x} - \frac{1-\alpha}{u-1} \ln \frac{1-\alpha}{\alpha} + \frac{u-1}{u} \right] \quad (15)$$

where $\frac{\partial \alpha}{\partial x}$ can be obtained from the equation (13) as,

$$\frac{\partial \alpha}{\partial x} = (1-\alpha) / \left\{ 1 + s - x - \frac{(u-1)e^{\gamma}}{\alpha(e^{\gamma}-1)(1+\omega)} \right\} \quad (16)$$

The molar volume of ice-I and ice-III, and the heat of transition from ice-I to ice-III are experimentally known as $V_I = 19.651$ c. c., ⁽⁵⁾ $V_{III} = 16.376$ c. c., ⁽⁶⁾ $\Delta E_t = 70 \pm 9$ cal/mole ⁽⁷⁾.

When the β -form is assumed to be ice-III, and taking the heat of transition from α -form to β -form to be equal to that from ice-I to ice-III, the value of V_β of 16.3941 c. c., the molar volume of the β -form in the liquid, can be obtained in the manner described below. The value of V_β obtained is almost equal to the value of ice-III, V_{III} , even the V_β as calculated is slightly greater. The result justifies the reasonableness of the assumption.

The following experimental values⁽⁸⁾ are used for the calculation. $I_A=1.0243 \cdot 10^{-40}$, $I_B=1.9207 \cdot 10^{-40}$, $I_C=2.9470 \cdot 10^{-40} \text{g} \cdot \text{cm}^2$, v_s ; 1595, 3652, and 3756cm^{-1} .

The parameters E_α , E_β , θ_α , θ_β and a at the triple point of ice-I, liquid water and the vapor can be obtained as follows.

Assuming the vapor behaves as an ideal gas at the triple point, the Gibb's free energy of the vapor, F_g , can be calculated from the equation

$$-\frac{F_g}{RT} = \gamma' + \ln V_g - 1 \quad (17)$$

where V_g is the molar volume of the vapor at the triple point.

Using the equilibrium condition of the three phases at the triple point, $F_g = F_l = F_s$, neglecting the values of $\frac{PV_l}{RT}$ and $\frac{PV_s}{RT}$ for their relative magnitude to $\frac{A_l}{RT}$ and $\frac{A_s}{RT}$, the following equation is obtained.

$$\ln \frac{V_g}{V_l} - 1 = \frac{1-\alpha}{1-u} \ln \frac{1-\alpha}{\alpha} + \ln \frac{u}{x} = 11.23717 \quad (18)$$

Substituting the equation (16) into the equation (15) and neglecting the value of $\frac{PV_\beta}{RT}$ at the triple point,

$$Z \equiv \frac{(e^y-1)(1+\omega)}{e^y} = \frac{u(1-\alpha) \ln \frac{1-\alpha}{\alpha} - (u-1)^2}{u(1-\alpha) + (u-1)^2} \quad (19)$$

When a certain value is assigned to V_β , α can be calculated from the equation (18). Then, for a given value of V_β and α , z can be calculated as the function of ω . For a given value of V_β and α , the calculated value of z must be equal to the value of the right hand side of the equation (19), if not, the assigned value of V_β in the equation (18) is adjusted and all the processes are repeated until the equation (19) is satisfied. For certain sets of V_β and α , two values of ω will satisfy the equation (19). However, for a given temperature and pressure the strain energy due to a vacancy cannot assume two different values at one time.

The single value of ω which will satisfy the equation (19) must be found. The calculation may be facilitated using the condition $\left(\frac{\partial Z}{\partial \omega}\right)_{V_\beta, \alpha} = 0$ for a given temperature, by differentiating the left hand side of the equation (19),

$$Z = \omega = e^y - 1 \quad (20)$$

After the values of V_β , α , and ω at the triple point, the value of n can be obtained by substituting them into the equation (9).

From the equations (13) and (14) the entropy of liquid water is given as,

$$\begin{aligned} \frac{S_l}{R} = & \left(\frac{\partial \psi T}{\partial T}\right)_v = \varphi - \frac{1}{u} \{ \sigma_\alpha - \theta_\alpha - 3(u-1) \\ & + \frac{s}{u} T \frac{\partial \alpha}{\partial T} \left[\varphi - (\gamma + \ln u) - \left(1 - \frac{1}{u}\right) \right. \\ & \left. - \frac{1}{s} \left\{ \ln \frac{1-\alpha}{\alpha} + \frac{1}{\alpha} \right\} \right] \dots \dots \dots (21) \end{aligned}$$

and

$$T \frac{\partial \alpha}{\partial T} = \frac{(1-\alpha)(u-1)(\theta_\beta - \theta_\alpha - \lambda)}{(e^y-1)(1+\omega)(1+s-x) \frac{u-1}{\alpha}}$$

where θ is equal to $-\sum_{i=1}^9 \ln(1 - \exp(-\theta_i/T)) + \sum_{i=1}^9$

$\frac{\theta_i/T \exp(-\theta_i/T)}{1 - \exp(-\theta_i/T)}$ for the respective forms and λ is

$$-\sum_{i=1}^9 \ln(1 - \exp(-\theta_{\beta i}/T)) + \sum_{i=1}^9 \ln(1 - \exp(-\theta_{\alpha i}/T)) - \frac{\Delta E_t}{RT}$$

The entropy of liquid water will be obtained from the equation (22),

$$\frac{S_l}{R} = \frac{S_g}{R} - \frac{\Delta S_v}{R} = \gamma' + \ln V_g + 3 - \frac{\Delta S_v}{R} \quad (22)$$

where S_g is the entropy of vapor and ΔS_v is the entropy of vaporization at the triple point, the latter being equal to 39.30 e. u. ⁽⁸⁾

Then, θ_α and θ_β can be calculated from the equations (13) and (21).

E_α is then determined from the equation (12a), E_β from $E_\beta = E_\alpha - \Delta E_t$, and a from the value of ω .

The calculated values are as listed in Table 1.

Table 1. Parameters and triple point properties.

$V_\alpha = 19.651 \text{c. c.}$	$V_\beta = 16.3941 \text{c. c.}$
$E_\alpha = 10773 \text{cal/mole}$	$E_\beta = 10703 \text{cal/mole}$
$\theta_\alpha = 217.87^\circ \text{K}$	$\theta_\beta = 210.77^\circ \text{K}$
$\Delta E_t = 70 \text{cal/mole}$	$\Delta S_v = 39.30 \text{e. u.}$
$n = 11.944$	$a = 0.14982 \cdot 10^{-3}$
$T = 273.16^\circ \text{K}$	$P = 0.0060294 \text{atm.}$

$V = 18.0188 \text{c. c.}$

Thermodynamic properties

For given temperatures the work function, A , are calculated using the equation (14) for the values of u . In every calculation of φ for the given value of u , α should have the value to satisfy the equation (13).

When the values of A thus obtained are plotted against the values of V for a given temperature becomes as presented in Fig 1.

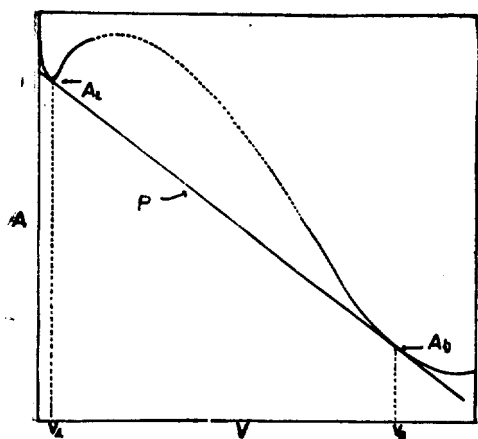


Fig 1. Schematic diagram of the Helmholtz free energy, A , vs volume at a given temperature.

Then, the slope of the common tangent line of liquid and gas gives the vapor pressure and the tangent points give the molar volumes of liquid and gas, respectively.

Entropy can be calculated from the equation (21).

The calculated molar volume of liquid water, vapor pressure and entropy of fusion and vaporization are listed in Tables 2, 3, and 4, respectively.

Table 2. Molar volume of liquid water.

T °K	V_{calc} c. c.	$V_{obs.}^{(5) (9)}$ c. c.	$\Delta\%$
273.16	(18.0188)	18.0188	
278.15	18.0151	18.0167	-0.01
283.15	18.0133	18.0214	-0.04
288.15	18.0137	18.0322	-0.10
293.15	18.0163	18.0484	-0.18
333.15	18.1152	18.3236	-1.14
373.15(T_b)	18.3706	18.7989	-2.28
423.15	18.9221	19.6408	-3.66
473.15	19.7575	20.8814	-5.38

Table 3. Vapor pressure.

T °K	P_{calc} atm.	$P_{obs.}^{(5) (9)}$ atm.	$\Delta\%$
273.16	(0.0060294)	0.0060294	
278.15	0.0085969	0.0086092	-0.14
283.15	0.012092	0.012177	-0.21
288.15	0.016793	0.016826	-0.20
293.15	0.023038	0.023072	-0.15
333.15	0.19838	0.19655	0.93
373.15(T_b)	1.0183	1.0000	1.83
423.15	4.770	4.698	1.53
473.15	15.202	15.341	-0.91

Table 4. Entropy of fusion and vaporization.

T °K	ΔS_{calc} e. u.	$\Delta S_{obs.}^{(5)}$ e. u.	$\Delta\%$
ΔS_f (273.16)	(5.297)	(5.257)	(0.76)
ΔS_v 273.16	(39.30)	39.30	
278.15	38.53	38.44	0.24
283.15	37.67	37.57	0.27
288.15	36.89	36.77	0.33
293.15	36.13	35.95	0.50
333.15	30.78	30.46	1.05
373.15(T_b)	26.42	26.05	1.42
423.15	21.96	21.44	2.43
473.15	18.35

Table 5. Critical point properties.

	T_c °K	P_c atm.	V_c c. c.
calc.	772.8	423.1	54.1
obs. (9)	647.4	218.3	56.3
$\Delta\%$	19.4	93.8	-3.91

Discussion

Generally good agreements between the calculated and observed values are observed for molar volumes of liquid, vapor pressure, and entropies of fusion and vaporization at various temperatures as illustrated by the listed tables.

The calculation shows the minimum molar volume to occur at 285.5 °K, while the observed minimum occur at 277.13 °K. The position of the minimum molar volume is largely dependent on the value of the heat of transition, ΔE_c . It is the contention of the authors, when the value of the heat of transi-

tion is properly taken within the limit of the probable errors of observations, that the calculated position of the minimum molar volume can be brought to a good agreement with the actual observation.

As expected, the fraction of the α -form decreases gradually as temperature rises. Relative amounts of each form in molar percentage are listed in Table 4.

Table 4. Contribution of the each forms in liquid water.

T °K	α -form	β -form	γ -form
273.16	48.56	51.20	0.24
278.15	47.51	52.08	0.41
283.15	46.64	52.80	0.56
288.15	45.61	53.64	0.75
293.15	44.60	54.46	0.94
333.15	36.89	60.20	2.91
373.15(T_b)	30.52	64.13	5.35
423.15	23.60	67.10	9.30
473.15	18.03	67.92	14.05

At the critical temperature, the α -form completely disappears. The fact simplifies the calculation of the critical point properties.

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